Appendix I. Chemical Analytical Method
MITC – sorbent tubes,
California Department of Health Services Laboratory

STAUFFER CHEMICAL COMPANY
RICHMOND RESEARCH CENTER
1200 S. 47TH STREET, RICHMOND, CA 94804

Method No. RRC-82-35 Date 8/26/82

Supersedes _____ Page 1

TITLE:

METHYL ISOTHIOCYANATE FROM METHAM-SODIUM DETERMINATION IN AIR

I. SCOPE

This method is designed to measure methyl isothiocyanate (MITC) in air. The method is applicable for methyl isothiocyanate concentrations between 0.01 and 6 mg per cubic meter in a 40-liter air sample. Methyl isothiocyanate is the active fumigant to which VAPAM® is converted upon application to soil.

.2 mg/ml = 120 mg/ml ✓

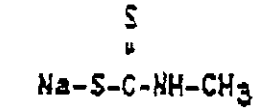
.01 mg/m³ = 3.3 ppb ; 6 mg/m³ = 2 ppm

II. SUMMARY OF METHOD

A known volume of air is drawn through a charcoal tube via a battery-operated sampling pump. The methyl isothiocyanate present in the air is quantitatively adsorbed on the charcoal. The charcoal is then desorbed with carbon disulfide; the extract is analyzed for methyl isothiocyanate by gas chromatography with nitrogen-phosphorus alkali flame ionization detection.

III. INTRODUCTION

VAPAM® soil fumigant, common name Metham-sodium, is sodium N-methyldithiocarbamate:



VAPAM® is generally formulated as an aqueous solution containing 32.7% anhydrous sodium salt and is nonvolatile. Its activity is due to decomposition to methyl isothiocyanate (CH_3NCS).

IV. APPARATUS AND REAGENTS

A. Apparatus

1. Gas Chromatograph. Hewlett-Packard Model 5710A or equivalent, equipped with a nitrogen-phosphorus alkali flame ionization detector (NP-AFID).

B. Reagents

1. Carbon Disulfide. Mallinckrodt AR grade, Cat. No. 4352 or equivalent.

2. Gases. Supplied to gas chromatograph via lines equipped with gas purification traps and suitable line regulators.

   a. Helium. High purity cylinder helium.

   b. Hydrogen. High purity cylinder hydrogen.

   c. Air. Dry air, free from organic contaminants, from cylinder or compressor.

3. Methyl Isothiocyanate. Analytical Reagent grade. Aldrich Cat. No. 11777-1.

IV. PROCEDURE

A. Air Sampling

Break both ends of the charcoal tube to provide openings for air to pass through. The smaller section of charcoal is used as a backup section and therefore is placed nearest the sampling pump. Use tubing from the sample tube holder to connect the back of the tube to the pump. Turn on the pump and set the flow rate to 100 mL/min. Calibrate the trap-pump assembly via RRC method 76-46; record the calibration data.

To take an air sample, support the charcoal tube in a vertical position with the sample tube holder and clip the trap to the employee's clothing so that the trap is located as close as possible to his or her breathing zone. Attach the pump to the employee via a convenient pocket. Turn on the pump, and take a 6-8 hour sample. At the end of the sampling period record the time. Remove the trap-pump assembly from the employee; recalibrate the assembly and record the recalibration data.

For sampling at relative humidity greater than 80%, connect a silica gel tube in front of the charcoal tube by means of a short tygon tubing during the entire sampling period. The silica gel is used as a drying agent preceding the charcoal to eliminate the effect of moisture (see Section VI.B.).

B. Gas Chromatographic Conditions

Set the temperature of oven, injection port, and detector on the gas chromatograph. Establish suitable flow rates for the various gases; optimizing the detector response according to the manufacturer's directions.

The following conditions are given for a Hewlett-Packard Model 5710A chromatograph with a N-P AFID detector and a 1.8 m x 2 mm i.d., 10% SP2250 column.

Column temperature:	95°C, isothermal
Injection port temperature:	250°C
Detector temperature:	300°C
Helium carrier gas flow:	30 mL/min
Hydrogen flow:	3 mL/min
Air flow:	60 mL/min
Quantitation:	digital integrator or data system; set attenuation to obtain a measurable peak from 0.5 ng of MITC.

See SAC for new Column

Under the above conditions, MITC elutes in approximately 2.4 minutes.

C. Calibration

Prepare five calibration standards containing 0.1, 1.0, 5.0, 10.0 and 20.0 micrograms of methyl isothiocyanate per mL of carbon disulfide to cover the desired range of calibration. Prepare standard solutions fresh weekly, and refrigerate standard solutions when not in use. Inject 5.0 microliters of each solution into the chromatograph at least twice and record the peak areas. Plot the average peak area against the corresponding MITC concentration (micrograms/mL), and draw the best-fitted straight line through the points. Check calibration periodically by occasionally alternating injections of standards with those of samples.

1 ng → 20 ng / 1 µl ←

D. Sample Analysis — SMALL CT · 100/50

Score each charcoal tube with a file in front of the glass wool plug and break the tube open. Remove the glass wool plug and place it in a 2-dram vial that contains 1.0 mL of carbon disulfide. Pour the charcoal in the front section into the vial, tapping the side of the tube to dislodge any charcoal that adheres to the walls. Immediately cap the vial with a polyseal-lined cap. Remove the separating foam plug

CT SIZE NOT STATED

and transfer the backup section into another 2-dram vial containing 1.0 mL of carbon disulfide; immediately cap the vial. Desorb the MITC for 30 minutes, agitating the sample occasionally to facilitate desorption.

1/2 50 CT — INCLUDED FROM THIS

Inject 5.0 microliters of the carbon disulfide extract from each section of the charcoal tube into the gas chromatograph. Dilute the extract if necessary to keep the response(s) within the range. Analyze the sample extracts immediately after calibration has been completed. If analysis of the extract cannot be completed on the same day, refrigerate the extract at 0°C. However, do not store the extract for more than 2 days due to the high volatility of carbon disulfide.

V. CALCULATIONS

A. Mean Flow Rate

Calculate the mean flow rate for the pump-trap assembly by the following equation:

$$F = \text{mean flow rate (L/min)} = \frac{A + B}{2}$$

where A = average initial flow rate, L/min
B = average final flow rate, L/min

B. MITC Concentration in Air

Use the calibration curve and the MITC peak area obtained from the sample extract to determine the amount of MITC in each section of the trap. Calculate the concentration of MITC in air by the following equation:

$$\text{MITC concentration } (mg/M^3) = \frac{(W1 + W2)}{F \times T}$$

where W1 = weight of MITC found in front section of charcoal tube, micrograms

W2 = weight of MITC found in backup section of charcoal tube, micrograms

F = mean flow rate, L/min
T = sampling time, minutes

VI. DISCUSSION

A. Precision and Accuracy

Desorption Efficiency (DE) for MITC was determined by introduction of known amounts of MITC directly into charcoal tubes at levels of 0.5, 5, 25, and 50 micrograms of MITC. (Six) replicates were prepared at each of the above levels. All samples were analyzed; the D.E. of MITC is shown in Table 1 (see Reference B for statistical procedure used).

The collection efficiency of this method was tested by generating MITC vapors with the use of the dynamic U-tube system adapted from the literature (References C & D). An average MITC recovery of 94% was obtained for 26 test trials with a relative standard deviation of 10%. Recovery data for MITC in air are shown in Table 2.

The present method was applied also to aqueous solutions of metham-sodium. In this recovery test, a known amount of metham-sodium in aqueous solution was injected onto moistened vermiculite placed at one end of the U-tube while air was pulled through the U-tube at 0.1 L/min and carried the MITC vapors into a charcoal tube at the other end of the U-tube. The presence of water and vermiculite is known to speed up the rate of decomposition of metham-sodium to MITC (Reference E). At the end of each sampling test, both sections of each charcoal tube were removed for desorption and analysis to obtain recovery of MITC. Under these conditions, at least 75% of metham-sodium (up to 190 ug) was converted to MITC in 5 hours. Longer time (16 hours) was required for the conversion of 380 ug of metham-sodium. A summary of the recovery data of MITC from metham-sodium in air is shown in Table 4.

B. Other Comments

The effect of humidity on the recoveries of MITC from air was also studied. A summary of recovery data from air of various relative humidities (R.H.) is shown in Table 5. No significant losses occurred when MITC was sampled at R.H. between 50% and 70%. However, at lower concentrations (less than 0.01 mg/M^3) and R.H. greater than 80%, humidity has a more serious effect (see Table 5). To avoid losses of MITC due to effects of moisture, the use of a silica gel tube preceding the charcoal tube is recommended for sampling at R.H. greater than 80%. Recoveries of MITC at high R.H. (>81%) with the use of the silica gel pre-trap showed no significant differences from recoveries at lower R.H. (see Table 6).

Experimentally no breakthrough was observed when 230 micrograms of MITC was adsorbed in the charcoal tube from air with 70 liters of air pulled through the tube at a sampling flow rate of 200 mL/min. This was determined by analysis of both the front and the backup section of the charcoal tube. In general, if more than 25% of the total sample is in the backup section, significant breakthrough may have occurred and the sample is not valid.

Storage stability tests indicated that recoveries of samples stored for 14 days under refrigeration at 4°C agreed within ±15% relative to those of initial samples (see Table 2).

VII. SAFETY PRECAUTIONS

A. Methyl Isothiocyanate

Methyl isothiocyanate is toxic, skin irritant and lachrymator.

Avoid contact with skin and eye.

Avoid inhalation of mist, sprays or vapors.

Use only with adequate ventilation and wear gloves.

B. Carbon Disulfide

Carbon disulfide is flammable and vapor harmful.

Keep away from heat and open flame.

Keep container closed.

Use only with adequate ventilation.

Avoid prolonged breathing of vapor.

Avoid prolonged or repeated contact with skin.

VIII. REFERENCES

A. WRC Notebook: 7397-34 to 50
7411-9 to 36
7550-25 to 44
7893-7 to 10

B. D. G. Taylor, R. E. Kupel, and J. M. Bryant, "Documentation of the NIOSH Validation Tests", DHEW (NIOSH) Publication No. 77-185, 1977.

C. L. W. Severs, R. G. Melcher and M. J. Kocsis, Am. Ind. Hyg. Assoc. J., 39, 321 (1978).

D. R. G. Melcher, R. R. Langer and R. O. Kagel, Am. Ind. Hyg. Assoc. J., 39, 349 (1978).

E. R. A. Gray and H. G. Strein, Phytopathology, 52, 734 (1962).

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Appendix A

A. Column Preparation and Conditioning

Wash inside of Pyrex column with 1% aqueous KOH and let stand filled with KOH solution 15 minutes. Rinse well with four successive methanol and two successive toluene washes. Fill column with a solution of 5% dimethyldichlorosilane in toluene and let stand 15 minutes. Drain and rinse with toluene. Finally, rinse with methanol and dry with a stream of nitrogen.

Pack the gas chromatographic column with the 10% SP 2250 packing under moderate vacuum with light tapping. Do not use a vibrator. The packing should not extend into the end areas of the column that are heated by the injection port and detector. Install the packed column in the chromatograph with the exit end free. Turn on the carrier gas to 20-40 mL/min, set the initial temperature to 80°C and hold it there for about 30 minutes. This will purge the column of oxygen and water vapor. Increase the column temperature at a rate of 2°C/min. The final conditioning temperature should be 240°C. Condition the column eight hours or more with 20-40 mL/min of carrier gas flowing. After conditioning, cool the oven and complete the installation of the column.

Table 2. Storage Stability of Methyl Isothiocyanate

Test 1			Test 2			Test 3			Test 4		
µg Taken	µg Found	% Recovery	µg Taken	µg Found	% Recovery	µg Taken	µg Found	% Recovery	µg Taken	µg Found	% Recovery
0.50	0.42[a]	84	5.14	4.71[a]	92	21.44	19.8[a]	92	51.45	52.3[a]	102
0.50	0.43[a]	86	5.14	4.93[a]	96	21.44	20.1[a]	94	51.45	53.0[a]	103
0.50	0.43[a]	86	5.14	4.86[a]	95	21.44	19.8[a]	92	51.45	51.1[a]	99
0.50	0.43[a]	86	5.00	4.60[a]	92	21.44	20.4[a]	95	51.45	50.6[a]	98
0.50	0.39[b]	78	5.15	5.16[b]	100	25.47	24.6[b]	97	51.45	50.1[b]	97
0.50	0.39[b]	78	5.15	5.19[b]	101	25.47	24.3[b]	95	51.45	45.3[b]	88
0.50	0.38[c]	76	5.15	4.59[c]	89	25.47	23.2[c]	91	51.45	46.8[c]	91
0.50	0.37[c]	74	5.15	4.71[c]	92	25.47	22.6[c]	89	51.45	55.6[c]	108
0.50	0.38[c]	76	5.14	4.11[c]	80	21.44	15.9[c]	74	51.45	44.9[c]	87
0.50	0.39[c]	78	5.14	4.01c	78	21.44	16.7[c]	78	51.45	45.7c	89

NOTES: a = Samples analyzed after being stored for 1 day under refrigeration
b = Samples analyzed after being stored for 7 days under refrigeration
c = Samples analyzed after being stored for 14 days under refrigeration
% Recovery not corrected for desorption efficiency (D.E.)

Table 1. Desorption Efficiency (D.E.) of Methyl Isothiocyanate

Formulation instead of G

Test 1			Test 2			Test 3			Test 4		
µg Taken	µg Found	D.E.	µg Taken	µg Found	D.E.	µg Taken	µg Found	D.E.	µg Taken	µg Found	D.E.
0.50	0.42	0.84	5.14	4.71	0.92	21.4	19.8	0.93	51.5	52.3	1.02
0.50	0.43	0.86	5.14	4.93	0.96	21.4	20.1	0.94	51.5	53.0	1.03
0.50	0.43	0.86	5.14	4.86	0.95	21.4	19.8	0.93	51.5	51.4	0.99
0.50	0.43	0.86	5.00	4.60	0.92	21.4	20.4	0.95	51.5	50.6	0.98
n =		4			4			4			n
Mean D.E. =		0.86			0.94			0.94			1.01
St. dev. =		0.010			0.021			0.0096			0.024
CV_1 =		0.012			0.022			0.010			0.024

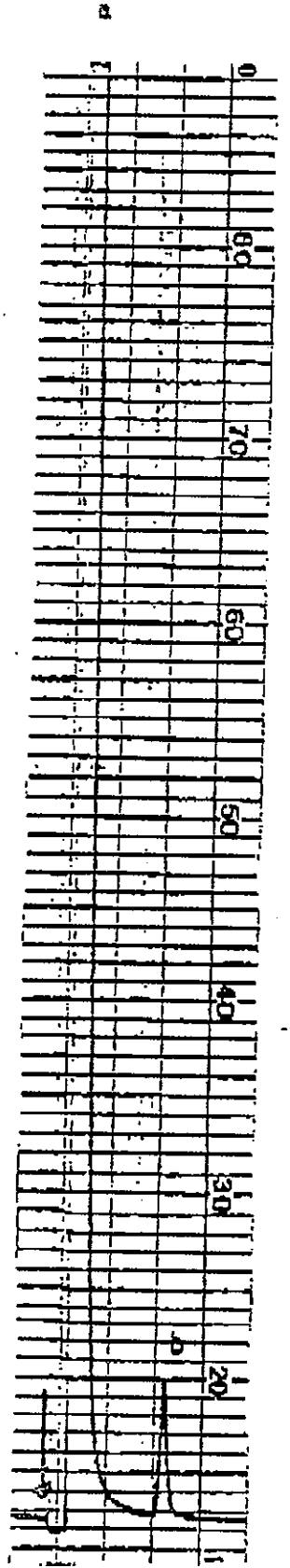
$\overline{CV}_1 = 0.018$

NOTES: CV_1 = coefficient of variation

$\overline{CV}_1$ = Pooled coefficient of variation.

FIGURE 1. Typical Chromatogram for MITC Analysis

Standard, 1 ug/mL



a = Solvent

b = MITC, 2.3 min.

Sample 7397-49-8, at 5.1 ug MIT

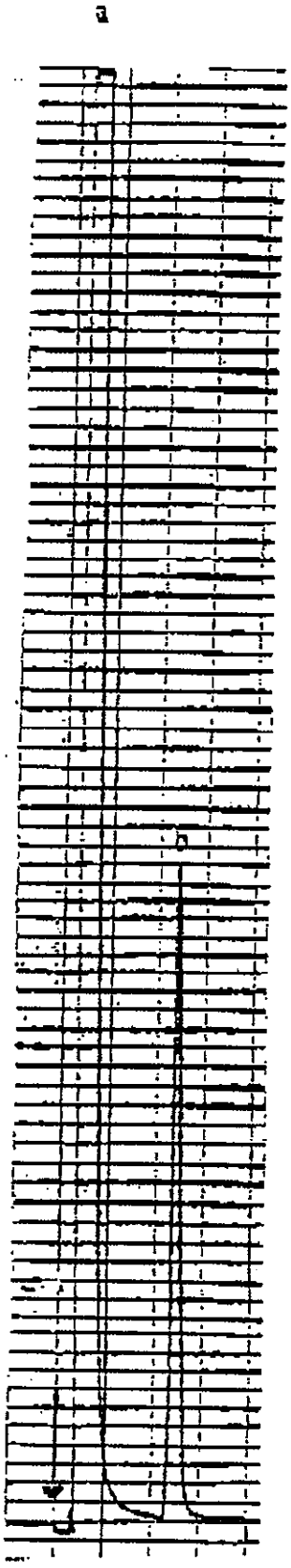


Table 3. Recovery Data for MITC in Air

Temperature = 65-68°F; R.H. = 58-70%

L/min Flow Rate	Minutes Sampling Time	Liters Air Volume	ug MITC Taken	ug MITC Found	% Recovery
0.1	430	48	0.5	0.44	88
0.1	430	40	0.5	0.44	88
0.1	430	45	0.5	0.44	88
0.1	510	47	0.5	0.36	72
0.1	510	52	0.5	0.37	74
0.1	510	53	0.5	0.39	78
0.1	410	40	5.15	4.20	82
0.1	410	40	5.15	4.49	87
0.1	410	43	5.15	4.72	92
0.1	380	36	5.15	4.71	92
0.1	420	39	5.15	5.34	104
0.1	430	44	5.15	5.05	98
0.1	420	40	10.29	10.9	106
0.1	460	43	25.47	27.3	107
0.1	460	47	25.47	25.7	101
0.1	460	45	25.47	26.0	102
0.1	450	50	25.47	25.3	99
0.1	450	42	25.47	25.2	99
0.1	450	48	25.47	24.2	95
0.1	360	38	51.45	46.9	91
0.1	370	37	51.45	48.6	94
0.1	460	45	51.45	48.5	94
0.1	450	46	51.45	53.4	104
0.1	460	46	51.45	49.5	96
0.1	390	38	51.45	50.6	98
0.1	450	47	227.4	207	91
0.2	370	71	227.4	195	86*
0.2	370	71	225.6	180	80*
0.2	370	66	225.6	179	79*

Mean = 94
RSD = 10%
n = 26

NOTES: % Recovery not corrected for desorption efficiency (D.E.)

* = Samples collected at flow rates greater than 0.1 L/min; not included in the calculation of mean % recovery

Table 4. Recovery Data for MITC from Metham-sodium in Air

L/min Flow Rate	Minute Sampling Time	Liters Air Volume	ug Metham-Sodium Taken	Theoretical ug MITC Taken	ug MITC Found	% MITC Found based on Theoretical MITC Taken
0.11	380	42	23.7	13.4	11.9	89
0.12	400	50	47.0	26.8	25.4	95
0.12	320	38	94.7	53.5	46.3	87
0.12	320	40	189.5	107.2	84.1	79
0.12	430	52	189.5	107.2	79.3	74
0.11	990	110	189.5	107.2	78.7	73
0.11	320	36	379.0	214.0	110	51*
0.11	440	48	379.0	214.0	99	46*
0.13	990	125	379.0	214.0	190	89

NOTES: * = low recoveries on these samples due to incomplete conversion of MITC from Metham-sodium.

Table 5. Effects of Relative Humidity (R.H.) on Recoveries of MITC from Air

Sampling Flow Rate = 0.1 L/min.

% R.H.	No. of Samples	Hours Sampling Time	Liters Air Volume	ug MITC Taken	% Recovery
58	3	7	40 - 48	0.5	88* (87 - 88)**
70	3	7	47 - 53	0.5	74 (71 - 79)
81	4	7	38 - 44	0.5	43 (32 - 57)
81	2	4	25	0.5	66 (59 - 72)
92	3	7	41 - 42	0.5	53 (41 - 63)
92	2	4	22 - 25	0.5	72 (70 - 75)
58	3	7	36 - 44	5	98 (92 - 104)
70	3	7	40 - 43	5	87 (82 - 92)
81	5	7	34 - 57	5	50 (44 - 58)
81	2	4	21 - 24	5	69 (66 - 72)
92	3	7	37 - 42	5	55 (48 - 62)
92	3	4	20 - 26	5	83 (78 - 89)
58	3	7	43 - 47	25.5	103 (101 - 107)
70	3	7	42 - 49	25.5	98 (91 - 99)
81	1	6	35	25.5	78
92	3	7	39 - 41	25.5	77 (73 - 82)
92	1	4	26	25.5	76
58	2	6	37 - 38	51.5	93 (91 - 94)
70	4	7	38 - 46	51.5	98 (94 - 104)
81	1	6	36	51.5	97
81	1	6	39	227.4	80
92	1	6	36	51.5	100
92	1	7	42	102.9	100
92	1	7	41	227.4	83

NOTES: * = Mean
** = Range
% Recovery not corrected for desorption efficiency (D.E.)

Table 6. Recovery Data for MITC in Air at High (>81%) Relative Humidity with the Use of Silica Gel as a Pre-trap for Moisture

Sampling Flow Rate = 0.1 L/min.

% R.H.	Hours Sampling Time	Liters Air Volume	ug MITC Taken	ug MITC Found	% Recovery
81	6	36	0.5	0.40	79
81	7	42	0.5	0.37	74
81	7	41	5	4.43	89
81	7	46	5	4.35	87
92	6	38	0.5	0.38	75
92	7	45	0.5	0.36	71
92	7	44	5	4.39	88
92	7	44	5	4.21	84
92	7	46	25	22.9	92
92	7	45	25	22.7	91
92	7	46	59	55.9	95
92	7	40	59	51.9	88

NOTE: % Recovery not corrected for desorption efficiency (D.E.)

METHOD RESOLUTION REQUEST

Res. #: MITC #2
Date 14 Oct 99

METHOD NO.: RRC-82-35

VERSION DATE: 26 Aug 1982

SECTION NO.: IV-C

PROBLEM: Calibration levels and standard prep in the original method do not reflect current lab sensitivity limits and preparative protocol. In the original method, standard solutions are prepared weekly, and refrigerated between uses. In the original method, the range of 20 to 0.1 µg/mL does not reflect routine detection limits of less than 0.05 µg/mL.

SUGGESTED RESOLUTION

Follow the EHLB MITC SOP for standard prep and calibration levels, including **daily** prep of working standards (also called "daily" standards) with no reuse on succeeding days; and follow ranges adhering approximately-to-exactly the range of 5.0 µg/mL to 0.025 µg/mL.

EHLB ANALYST _____ DATE _____

APPROVED RESOLUTION

REPRESENTATIVE _____ DATE _____

METHOD RESOLUTION REQUEST

Res. #: MITC #3
Date _____

METHOD NO.: RRC-82-35

VERSION DATE: 26 Aug 1982

SECTION NO.: IV-B

PROBLEM: Original method calls for packed column use.

SUGGESTED RESOLUTION

Follow the EHLB MITC SOP to allow use of other columns via the establishment of equivalence to the original method.

_____ _____
EHLB ANALYST DATE

APPROVED RESOLUTION

_____ _____
REPRESENTATIVE DATE

METHOD RESOLUTION REQUEST

Res. #: MITC #4
Date 15 Oct 99

METHOD NO.: RRC-82-35

VERSION DATE: 26 Aug 1982

SECTION NO.: IV-B

PROBLEM: Wording of the original method does not allow for establishment of equivalence in performance using parameters other than those listed in the written method. Since 1982, GC has changed in many of the mechanics which employment may improve sensitivity and reproducibility of samples and the standards used to quantitate and validate the instrument. Demonstration of equivalence is acceptable in EPA CLP methods, to substitute a replacement technique for an approved technique.

SUGGESTED RESOLUTION

For MITC analysis, follow the SOP which has a provision allowing for demonstration of equivalency in results to those obtained by the original methodology.

EHLB ANALYST DATE

APPROVED RESOLUTION

REPRESENTATIVE DATE

METHOD RESOLUTION REQUEST

Res. #: MITC #1
Date 14 Oct 99

METHOD NO.: Stauffer RRC-82-35

VERSION DATE: 26 Aug 1982

SECTION NO.: IV-B

PROBLEM: Carbon Disulfide (CS_2), used in the method to desorb & analyse MITC, irreversibly degrades the bead probe composing the major functional unit of Nitrogen-Phosphorus Detector. This can lead to difficulties in quantitative curve linearity, curve and sample sensitivity and precision.

SUGGESTED RESOLUTION

Replace CS_2 with solvent tested by Zeneca (see attachment 14 Feb 95) and Dept. of Pesticide Regulation (DPR), as follows:

Ethyl Acetate, pesticide or better grade, to CS_2 (pesticide or better grade), 1000/1.

Validation data will be provided on request for comparative purposes.

EHLB ANALYST _____ DATE _____

APPROVED RESOLUTION

REPRESENTATIVE _____ DATE _____

ENVIRONMENTAL HEALTH LABORATORY BRANCH
CALIFORNIA DEPARTMENT OF HEALTH SERVICES

STANDARD OPERATING PROCEDURE

Title: Methyl Isothiocyanate Determination in Air	
Analyte: Methyl Isothiocyanate (CAS 556-61-6)	SOP/Rev. No: DPR/Stauffer/ RRC-62-35/R0
Matrix: air	Date Revised: NA
Date Issued: 1/28/99	Effective Date: 3/1/99

1. Principle and Applicability of the Method

Methyl Isothiocyanate is the active component of Metam-Sodium, a soil fumigant. This method is designed to measure Methyl Isothiocyanate (MITC) in air. Charcoal sorbent air-sampling tubes are opened and the charcoal desorped in appropriate solvent. Analysis is by gas chromatography equipped with Nitrogen-Phosphorus detector (GC-NPD).

1.1 The method is applicable to the determination of MITC in air samples under the CARB Environmental Monitoring Program.

1.2 Use of this method is restricted to analysts who are knowledgeable in the principles and operation of gas chromatography with Nitrogen-Phosphorus detectors, and associated chemical, chromatographic, molecular and physical interferences. The analyst must have demonstrated knowledge of this method and successful analysis of blind quality control and other check samples prior to independent analyses using this method.

2. Range and Sensitivity

Procedure has an established Method Limit of Detection (MLOD) of 0.030 µg/sample. Reporting limits (RL) are the lower and upper limits of calibration at 0.075 µg/sample and 3000 µg/sample respectively. Day-to-day LOD may be expected to range between 0.030 µg/sample and 0.120 µg/sample. Linearity expressed as correlation coefficient of regression analysis exceeds 0.9900.

3. Safety Considerations

3.1 Before initial demonstration of competency in performance of the Method, analyst has demonstrated that she/he has read and agrees to follow the procedures as written in the Environmental Health Laboratory Branch (EHLB) Health and Safety (H & S) Manual, by signing the accompanying statement included with the manual, and left with the Branch Health and Safety Officer.

3.2 Additional training and information in the handling of carbon disulfide (CS_2) has been given by the Lab H & S officer.

3.3 No known carcinogenic, mutagenic, or teratogenic materials are used in this method. Analysts have been shown the MSDS for each chemical used in this procedure prior to starting work.

4. Interferences

Water coincidentally captured during sampling appears as droplets clinging to desorption vial walls. Humidity effects on MITC have been presented in the original method (1). Silica gel was recommended as front-end water capture, when sampling site R.H. exceeds 80%. Studies on humidity at concentrations

California Department of Health Services
Environmental Health Laboratory
2151 Berkeley Way
Berkeley, California 94704
STANDARD OPERATING PROCEDURE
METHYL ISOTHIOCYANATE IN AIR

SOP #
Previous SOP: none

DRAFT

4. Interferences

lower than 0.5 µg/mL have not been performed. No modifications have been made to method to compensate for water-presence effect on quantitation.

5. Equipment and Supplies

Instrumentation

Gas chromatograph with modules capable to achieve and sustain performance characteristics specified by the method.

5.1 Detector
Nitrogen-Phosporus Detector able to achieve a Nitrogen:Carbon ratio of at least 3:1 with 4:1 preferable.

5.1.1 Injector
Capillary column design, with splitter.
5.1.2 Column:
Capillary, any capable of meeting performance criteria. J & W DB-5, 30 m, 0.25 mm i.d., 1.0 µ film has proven acceptable.
5.1.3 Autosampler
Any capable of meeting performance criteria. Leap CTC A200SE has proven acceptable.
5.1.4 Data Collection
Integrator or computer-based system capable of acceptable baseline and peak integrations. Perkin-Elmer Turbochrom software has met performance criteria.

5.2 GC Temperatures (°C)

Detector: 300°
Injector: 200°
Column: 40° to 70° @ 5°/min (time: 6 min.), 70° to 220° @ 15°/min, total run time 16 min.
Retention time, MITC: 5.7 minutes.

5.3 GC Pneumatics

5.3.1 Carrier: Helium, 99.999% purity mandatory. Pressure 80 psi. Flow 25-45 cm/sec linear velocity (acetonitrile headspace injection), @ 70°.
5.3.2 Make-up: Helium recommended, 99.999% purity mandatory, source may be same as for carrier. Pressure 60 psi. Flow: up to 30 mL/min
5.3.3 Air: ultra-zero mandatory, Pressure 60 psi. Flow 175 mL/min or to achieve 4/1 N/C.
5.3.4 Hydrogen: from generator, or 99.999% purity if from cylinder. Pressure 40 psi. Flow: 4 mL/min or to achieve 4/1 N/C.

5.4. Labware

5.4.1 GC flow measuring device.
5.4.2 Analytical balance for preparation of stock standard from crystalline MITC.
5.4.3 Explosion-proof refrigerator for storage of standards, CS_2.
5.4.4 Explosion-proof refrigerator (not the same one as for standards) for storage of desorped samples.
5.4.5 Glassware & related items: volumetric flasks, TD volumetric pipettes; 5 ¼ in. glass disposable Pasteur pipettes; 3.7 mL disposable glass vials with open-hole caps and TFE/rubber seals, 1.7 mL Varian type autosampler vials, with seals and caps.
5.4.6 Hamilton syringes.
5.4.7 Charcoal tube tools: scribers, glass-wool pullers, caps.
5.4.8 Sorbent tubes: SKC cat. No. 226-09, 8 x 100 mm, 200/400 mg, coconut charcoal.
5.4.9 Vial vibrator and vial racks.

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6. Reagents and Standards

6.1 Carbon Disulfide, low Benzene grade, EM Omnisolve cat. # CX-0397-6, 500 mL size. A special order item not listed in VWR catalog. VWR has stocked this item and EHLB has ordered stock from them. Equivalent purity of another vendor is acceptable, but items have proved 2-4x more costly. New lots from any vendor must be checked for purity by GC injection, before signing off on order as acceptable.

6.2 Toluene, Pesticide/Residue Grade or better.

6.3 Methyl Isothiocyanate

6.3.1 Prepare from crystalline solid of the highest obtainable purity (minimum 95%) obtained from reputable manufacturer. Aldrich and Fluka are two souces, which have listed MITC purity at greater than 95%. The ordering and use of liquid and diluted solutions as stock source is discouraged at EHLB.

6.3.2 **Quality Control stock:** Follow the procedure recommended by Environmental Lab Accreditation Program (ELAP), and use crystalline MITC obtained from separate manufacturers, in the preparation of a separate stock for QC and check standards, than that used for calibration standards.

6.3.3 Storage, volatility and toxicity of crystalline MITC.
6.3.3.1 Store in standards-designated freezer when not in use. Store under nitrogen.
6.3.3.2 MITC sublimates from the crystalline to gaseous state at room temperatures, and the weighing analyst must take this into consideration when preparing stocks.
6.3.3.3 Toxicity of MITC. MITC is highly toxic. Perform all transfers of crystals to holding container within a hood capable of achieving 100 lfpm (as checked and tagged within the past year). Never transport a container holding crystalline MITC outside of hood, without the container being firmly sealed and capped. All weighing done outside of hood of crystalline MITC is to be done in a capped, sealed container. SKC-type 1-dram and 2-dram (4 mL/8mL) vials with solid, TFE lined caps, make acceptable weighing and stock solution containers. Alternatively, a volumetric flask with ground glass stopper may be used for weighing with the stopper kept on between additions of MITC (see 6.3.4). The containment vessel for the crystals as transferred from hood to flask or vial must remain capped except for the moment of transfer.

6.3.4 Stock Solution Standards Preparation for Calibration, D.E. and Quality Control
6.3.4.1 Stock Solution for daily calibration standards. Using a scale labelled to have been calibrated within the past year, capable of readout to at least **four** decimal places. Mettler AT400 balance ser. # 1116020029, state tag #1005108, has met these requirements. Weigh out enough MITC to prepare at least **3 mL** stock, at a concentration to prepare the daily high calibration standard no higher than 10 µg/mL. Example: prepare stock standard of 10 mg/mL by weighing out 50 mg crystalline MITC into a tared 8 mL SKC-type vial (amber preferred, vial tared with cap on) into which a small volume of Toluene has been added (vial has been tared with this volume). The vial has been previously marked to indicate the 5 mL level. When the 50 mg weight is achieved, cap the vial, move vial to hood, bring Toluene volume to mark, and gently mix by swirling or use vortex mixer. Initial, label and date the vial, including mfr. lot # of MITC. Store in standards-designated freezer between use. Record in lab notebook.
6.3.4.2 Stock Spiking Solution for Quality Control. Prepare to deliver µl volume into 3 mL solvent. Use the same spiking solution to deliver µl volume into charcoal, which will be desorped with samples.
6.3.4.3 Stock Spiking Solution for Desorption Efficiency (D.E.). Prepare from same stock solution as used for the daily standards. Prepare at a concentration and volume to deliver a target amount into charcoal at the upper range of the calibration curve. Prepare to deliver a syringe volume into charcoal not to exceed 25 µL.

6.3.5 Replace stock standards solutions monthly. Formal studies of degradation of accuracy of MITC stock in Toluene over time have not been performed.

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7. Sample Collection, Preservation, Shipping and Storage

7.1 Chain-of-Custody.

Discuss with the collecting staff the forms and procedure for maintenance of Chain-of-Custody documentation within QA protocols.

7.2 Sample Collection

Capture: SKC tube, catalog # 226-09, coconut charcoal 400/200 mg. 2 L/min has been determined the maximal flow with no breakthrough at the SOP quantitative levels. Discuss the sample collection protocol with the collecting staff. An example of sample train is provided in reference 2.

7.3 Sample Shipping

Discuss the sample shipping protocol with the collecting staff.

7.4 Sample Intake

With another staff member, cross-check the sample identification on the sample tubes with the chain-of-custody and EHLB Analysis Request forms. If a sampling staff member delivers the samples, assistance of sampling staff with check-in is a MANDATORY REQUIREMENT. Initial all forms by all staff performing the samples intake.

7.5 Sample preservation

Degradation study of MITC has been performed by EHL, indicating a short (approximately 2 weeks) hold time before analysis is required. Discuss the sample preservation protocol with the collecting staff, to indicate steps to minimize preanalysis hold time. Immediate storage on dry ice after sampling has been utilized.

7.6 Sample and Extract Storage

Store CS_2 extracts up to 6 months. Dispose of unanalysed samples after 2 months.

8. Quality Control

8.1 Solvents

Analyse new lots before use, and keep a copy of the results on file, recording on the results the manufacturer and lot number. Record in lab notebook solvent manufacturer & lot number, the date each bottle was received, the date each bottle was opened. On the solvent label initial and note the received and opening dates.

8.2 Standards

Prepare from crystalline stock purchased within one year of analysis. Label bottle with analyst initials, date received and date opened. Specify on the label if a particular bottle is dedicated for a particular analysis only. Record manufacturer and lot number in lab notebook.

8.3 Reference Materials and refereed analyses

NIST does not provide SRM for MITC. Department of Pestidice Regulation has performed analyses of spikes and standards as a cross check of accuracy.

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8. Quality Control

8.4 Injection Protocol

8.4.1 Frequency. Perform all injections in duplicate.

8.4.2 Standards. Run a complete standard curve at least at the beginning and at the end of each analytical day or the end of the sample batch. Run a single standard at intermediate concentration as a check standard every 10 samples.

8.4.3. Quality Controls. Run a solvent quality control sample after every 10 sample injections. Since samples are injected in duplicate, this is equivalent to 2 Q.C. injections per every 5 sample injections. Run charcoal spike quality control sample at the same interval. Include field and trip quality control spikes as part of the analytical batch.

8.5 Spikes.

Charcoal spikes, as trip spikes and field spikes are provided by EHLB to sampling staff as part of the sampling protocol. Blank tubes and blank spikes are considered as part of the spike set provided. Spike standard is available to sampling staff on request, including for on-site spiking. Solvent Q.C. spikes are performed as part of the daily analysis and provided to sampling staff on request.

Archive sets of trip spikes and field spikes are prepared at the same time in the same fashion as the trip spikes, and remain in lab for internal analysis.

8.6 Blanks

Solvent blanks form the zero-point of the calibration curve and are included as part of the routine standard curve analysis. Trip and field spike sets include appropriate charcoal and solvent blanks.

8.5 Analytical Run Acceptance/Rejection Performance criteria

8.6.1 Warning Limits. Data questionable. Stop analysis and consult supervisor if any of the following conditions exist:

TSD N/C ratio < 3/1: Add comment citing condition for all analyses on all days in which condition exists.
Correlation coefficient (r^2) of either of the two daily analytical standard curves < 0.990: accept results for the half of the analytical day which were quantitated under the acceptable ($r^2 > 0.990$) curve. Question results quantitated by the half of the analytical day which $r^2 < 0.990$.
Quality Control Injections (charcoal/solvent spikes): Initial quality control injection. If initial Q.C. injection, performed immediately upon the initial injections of the first daily curve, fails to achieve ± 80% of target value, reinject from same vial. If this first reinjection achieves ± 80% target value, repeat the injection to check precision. If the first reinjection gives a value failing to achieve ±80% target value, at analyst discretion, either prepare a new solvent Q.C. or prepare a new daily standard set. Advise supervisor of the adverse conditions. Within-analysis quality-control injections. If one Q.C. injection of two from a particular vial, exceeds warning or control limits on the entire analytical day: accept all. One Q.C. vial (2 injections) exceeds warning limits, but values fall within control limits: accept all with comment. If two or more Q.C. run in consecutive order exceed warning limits, but fall within control limit values, conditionally accept results analysed between the two Q.C. vials (4 injections) with comment. If one Q.C. vial (2 injections) exceeds warning limits but falls within control limits, AND the check standard

immediately preceding or following gives one or both injection values exceeding ± 25% of the expected quantitation against its closest calibration curve, question all succeeding

8. Quality Control

sample values until the Q.C. values fall within warning limits AND check standard values (one complete vial injection set) fall within ± 25% of the expected quantitation.

8.6.2 Control Limits. Data out of control. Stop analysis and report results to supervisor. Determine which results may be reportable. Prepare a corrective action report (CAR) and determine source of out-of-control condition. Initiate steps to correct the condition. Any of the following is an out of control conditon:
TSD N/C ratio < 2/1;
Correlation coefficient (r^2) of both of the two daily analytical standard curves < 0.990.
Quality Control injections (charcoal/solvent spikes): if both Q.C. injections from only one particular vial, exceeds control limits out of the entire analytical day: conditionally accept results immediately following the injections of the out-of-control Q.C. If one Q.C. vial (2 injections) exceeds warning limit in one direction (+ or -), and the succeeding Q.C. vial exceeds warning limit in the other direction, but values fall within control limits: conditionally accept all with comment. If two or more Q.C.s run in consecutive order exceed control limits, stop analysis and initiate corrective action as indicated above. If one Q.C. vial (2 injections) exceeds control limits, but the following Q.C. vial injections give values within warning limits, and the succeeding Q.C. vial injections give values beyond the control limits (Q.C. injections from 3 separate vials): stop the analysis, initiate corrective action as indicated above, and consult with supervisor concerning which sample injections may be conditionally acceptable. If the check standard immediately preceding or following gives one or both injection values exceeding ± 25% of the expected quantitation against its closest calibration curve, and the closest Q.C. injections (one or both from same vial) give value(s) exceeding control limits: stop further analyses, initiate corrective action, and consult with supervisor as above to determine acceptability of questionable data.

Other warning or control limit conditions not covered above: consult with supervisor.

8.7 Desorption Efficiency (D.E.)
8.7.1 Run once prior to immediate field sampling, or every six months if continuous lab analyses exceed six months.
8.7.2 Prepare D.E. injection stock from the same master stock as used for the daily calibration curve prep.
8.7.3 Prepare D.E. charcoal spikes for at least 5 levels, and D.E. blank.
8.7.4 Include all Q.C. and check standards as per field samples analysis protocol above. The same Q.C. reject/accept performance criteria apply as for field samples analysis.

8.8 Method Limit of Detection (MLOD)
8.8.1 Run once prior to immediate field sampling, or every six months if continuous lab analyses exceed six months.
8.8.2 Follow the 40 CFR Pt. 136, App. B protocol of 7 injections of a single vial preparation, of a sample target value at or just above the lower quantitation limit.
8.8.3 Include all Q.C.s as per field samples analysis protocol above. The same Q.C. reject/accept performance criteria apply as for field samples analysis.

9. Instrument Calibration and Preparation of Daily Standards

9.1 Initial Instrument Calibration. Equivalent to achievement of N/C ratio of 3/1 for optimal Nitrogen-compound sensitivity and detection. Follow the instrument manufacturer protocols for conditioning and optimization of bead probe (attachments). Determine the column linear velocity at the eluting temperature of the (first) analyte of interest. Note all

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results in lab notebook and instrument logbook. Keep a copy of the chromatography report with chromatogram documenting the calibration with the analysis file.

9.2 Daily Calibration of Instrument.

9.2.1 Daily shutdown of instrument. If stopping analyses but GC remains in good operational mode: Turn off the detector. Shut off hydrogen and air (turn off at tank and/or at external valving. Do not turn on/off the needle valves located in the GC, which are delicate and easily misaligned, changing the flow settings). Turn the bead power amperage to minimal "on" (dormant) current. Leave bead probe power on. Put GC in this mode when performing routine maintenance such as changing columns and septa.

9. Instrument Calibration and Preparation of Daily Standards

9.2.2 Daily startup of instrument. Turn on the detector. Open the hydrogen and air lines. Recheck the current through the bead probe. Let the bead probe sit at the dormant current 15 minutes with the hydrogen and air on. Then, increase the current to the operating current in 25 % increments, holding at each 25 % increment 15 minutes to allow bead to stabilize, minimize degradation and possible bead fracture. Once operating current is reached, wait an additional 15 minutes to allow bead to stabilize before making injections. Consult the manufacturer protocols as necessary (attachment).

9.3 Standard Prep. Serial dilution protocol is performed as follows:
-Remove CS_2 from freezer and allow to equilibrate to room temperature.
-To a suitable volumetric flask partially filled with CS_2, add the volume of MITC stock standard required for the highest calibrator. Bring to mark with solvent, cap, mix and mark flask with the concentration and analyte name
-Using TD volumetric pipettes, prepare the lower calibrators, by adding the required volume of the higher daily standard to a vol. flask partially filled with CS_2, and continuing as before.
-Previous analyses have had a calibration range of 5 µg/mL to 0.025 µg/mL.

9.4 Quality Control Prep. The same Q.C. stock is used for both the charcoal Q.C. spiking (prep the day before analysis) and the solvent Q.C. For the charcoal Q.C. spike, desorp and analyse with the samples. For the solvent Q.C., analyse a first injection immediately after the first injections of the first standard curve of the day.

9.5 Aliquot standards and Q.C. to autosampler (A/S) vials. Analyse the standards and Q.C. by autosampler or hand injection.

9.6 If calibration point(s) area counts show significant deviation from the expected values, prepare a new calibration point or new standard set at analyst discretion. Note repeated incidence of unexpected area count results for standards.

9.7 Performance of samples analyses is contingent on standard curve and Q.C. meeting initial daily quality control criteria (8.6.1). Therefore, do not desorp samples until analyst has examined the initial curve and Q.C. results.

9.8 Curve degradation. CS_2 is known to degrade performance of the TSD bead over time, including observable significant area count reductions of same standards within an analytical day. Therefore, it is not considered actionable that standard curve values between the first curve and subsequent curves on the same analytical day do not agree closely. Within-curve statistical values must meet the quality control criteria of the SOP.

9.9 Blanks. Blank contamination has not been a significant source of performance impairment in MITC analysis. Should an interfering peak occur in a blank, prepare another blank and inject. Should the problem recur, stop the analysis and discover the source of the contamination.

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10. Samples Preparation and Analysis

Perform all operations where chemicals are used in a hood rated within the past year to deliver 100 lfpm.

10.1 Set up a ring stand with apparatus to hold a small glass funnel with bore of sufficient diameter to allow free passage of charcoal. With an empty 3.7 mL (1-dram) SKC-type vial in place on the stand base, adjust funnel so that its bottom stem opening is just below the vial mouth, such that all charcoal flowing through the funnel must fall into the vial even if some particles collide with vial walls, and rebound in a vector opposite to gravity (up).

10.2 Using TD volumetric pipette, add 3 mL CS_2 to the number of 3.7 mL (1-dram) SKC-type vials sufficient to desorp all samples to be analysed on the analytical day. Cap with open-hole cap with TFE/rubber seal.

10.3 Put filled vials on agitator rack, and place in samples only freezer for 15 minutes minimum. Optional: freeze a small cold pack overnight or longer, and pre-chill a clean cardboard box, large enough to hold a small cold pack and the sample rack with vials. Use the box, with cold pack, to hold the chilled vials by the workhood during the desorption.

10.4 Cross check sample i.d. on sample tube with the sample i.d. on the chain of custody or lab analysis request form.

10.5 Retrieve one of the chilled vials prepared in step 10-1 above, from either the chilled box with cold pack kept for the entire procedure in the hood, or from the freezer. Uncap the vial (retain the cap), and place under the funnel stem to receive the charcoal.

10.6 Uncap the sample tube, remove glass wool or (if uncapping from the tube rear) foam retaining material and discard.

10.7 Either decant the sampled charcoal into a clean SKC-type 1-dram vial, then slowly pour charcoal onto funnel, or directly decant the sampled charcoal from the sampling tube slowly onto the funnel. Recap the vial (use the same cap). Transfer the sample label from the tube if possible, or label the vial with the sample I.d., analysis identifier, date and preparing analyst's initials. Mix the contents by gentle swirling or vortex mixing, and place vial onto agitation rack.

10.8 After all vials are prepared in the same fashion, transfer the rack to the agitator. Set the time for 30 minutes and begin the agitation.

10.9 After agitation/desorption has been completed, move rack back to hood. Realiquot sample-containing desorbing solution into at least two portions, using disposable 5 ¼" Pasteur pipettes, into 1.8 mL (autosampler, a/s) vials. Label each a/s vial with sample I.d., analysis identifier and date. Indicate for the sample i.d. if the charcoal is from the front or back of tube. One vial is designated the backup or archive portion, and stored in samples refrigerator for possible later reanalysis, in the EHL facility or by a third-party lab.

10.10 Analyse the non-backup portion(s) by hand or autsampler injection. Perform duplicate injections from the same vial.

10.11 Sample concentrations exceeding the highest calibration standard must be diluted and reanalyzed. Notate which samples must be reanalysed, and the reason. If dilution is performed, notate and write on the dilution vial, the dilution prepared (1/100, 1/1000, etc.), as well as the sample identifiers as in 10-9. Use Hamilton syringes to prepare dilutions, not Gilson or other pipettors having greater inherent inaccuracies and contamination issues.

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10. Samples Preparation and Analysis

10.12 If known sample duplicates, or duplicate injections, give results not within 75% of each other, inform the supervisor and obtain prior permission to analyse the backup. If the backup vial injections do not agree with any of the previous injections, or any two injections again do not agree within 75%, do not reanalyse. Report all results.

11. Calculations and Reporting

11.1 Quantitation.

Quantitations are obtained from linear regression standard curve, as follows:

$$x = \frac{(y-b)}{m}$$ where

y: the instrument output (area counts)
b: the y-intercept
m: the slope of the standard curve
x: the concentration obtained by the funct
(note: other variables may be used to refer to slope and y-intercept).

In routine lab operations, preliminary quantitations are obtained directly from the Turbochrom data collecting software. Run identifiers and area counts are then exported into Microsoft Excel (Excel) using comma-separated-variable (. csv) format generated by the Turbochrom Summary Report Editor. Reported results are obtained by using Excel linear regression functions and analyst data handling.

Document the required calculation(s) from sample preparation and the original instrument readings to the final sample concentration. Where applicable, a sample calculation may be demonstrated. Describe any forms, spreadsheets and/or data reduction systems to be used to reduces, calculate, and/or record results.

11.2 Desorption Efficiency

Obtain the amount desorbed by analysis of the charcoal medium, using functions of section 11.1. Generate a standard curve using Excel, plotting the amount analysed on the y-axis, vs. the amount put onto the charcoal on the x-axis. The D.E. blank is included in the curve determination. The t-statistic (t) generated by the regression analysis performed to make the resultant line, is compared to two-tailed t-table statistic (T) at the 95% confidence level, for n-2 degrees of freedom. If the absolute value of t is less than the T-table value, there is no significant difference between the origin and y-intercept at the confidence level examined. The slope of the calculated curve gives the D.E., which is assumed to be linear throughout the range for which the D.E.s were performed.

If the absolute value of t is greater than the T-table value, a significant difference exists between the y-intercept and the origin, and the slope is rejected as a D.E. determinant. The sum of the MITC amounts as analysed is divided by the amount of MITC put onto the charcoal (Σ_y/Σ_x), giving an overall desorption efficiency which is adequate for reporting but does not indicate deviations from linearity between desorption concentration points or ranges of points.

11.3 Quality Control

$$\text{Recovery (\%)} = \frac{\text{amount analysed}}{\text{amount input}} \times 100.$$

Mean of two injections from same vial can be included. but each injection counts as a single quality control value.

11.3.1 Rejection Criteria.
Reject Q.C. if injections from both vials do not have a coefficient of variation (C.V.) less than 25%. Reinject Q.C. if possible. If not possible (overnight unmonitored analyses), reject subsequent analyses closest to the questionable Q.C. following the out-of-control protocol of 8.6.2.
Warning Limit: greater than 2 standard deviations (s.d.) or 10% (whichever is greater) from the target value, but less than 3 s.d. or 15% (whichever is greater). Follow Shewhart's Rules (attachment) concerning Q.C. results at different warning levels.
Control Limit: greater than 3 s.d. or 15% (whichever is greater) from the target value. Segregate all runs subsequent to questionable injection, following the out-of-control protocol of 8.6.2.

11.3.2 Incorporate Q.C. results in Lab Q.C. Control Charts.

11.4 Significant figures.

Report results to 3 digits, 4 significant figures.

11.5 Results Reporting

11.5.1 Injection Results
11.5.1.1 Analyte Present Within Quantitative Limits. For sample injections having peaks at the MITC retention time, within the calibrated range, report analysis results in µg/mL (micrograms per milliter) units. Analysis result consists of the mean of 2 sample injections from the same vial onto GC. Report results per analysis ± plus or minus the product of the result times the coefficient of variation between injections of the same vial.
11.5.1.2 Analyte Detected But Not Quantitated. For sample injections having peaks at the MITC retention time, below the Limit of Quantitation (LOQ) but above the Limit of Detection (LOD), report results as "MITC < [list the LOQ value]LOQ."
11.5.1.3 Non Detect. Report injections (including true blanks) where the analyst and the data collection software identify no peak with a quantification above the detection limit at the retention time of MITC, as "ND" — Not Detected. (On first use, use the term; ND (Not Detected). Specify the detection limit. Use "LOD" in place of "Limit of Detection." (On first use, use the term; "LOD (Limit of Detection.")
11.5.2 Sample Results. A "Sample" for results reporting purposes, is the mean of two (or more) injections from the front OR back of a single sample tube, in the desorbing volume 3 mL.
11.5.2.1 Analyte Present Within Quantitative Limits. Follow the protocol of 11.5.1.1, but report sample results as "µg/sample." Results as µg /sample will usually be 3 times results as µg/mL, since sample results are usually per 3 mL.
11.5.2.2 Analyte Detected But Not Quantitated. Follow the protocol of 11.5.1.2, listing the LOQ per sample, which will be higher than the LOQ per injection.
11.5.2.3 Non Detect. Follow the protocol of 11.5.1.3, listing the LOD per sample. which will be higher than the LOD per injection.
11.5.3. Limit of Detection. Use the daily limit of detection achieved on the day sample was analysed as the reporting limit of detection. Do not use the Method Limit of Detection for results reporting .
11.5.4 Other. If sample was diluted to quantitate within calibrated range, report the corrected quantitation. Also specify dilution prepared in final report, but not on the EHLB reporting sheet.
If sample could not be suitably prepared for GC injection, report as "UFA". Unsuitable For Analysis. (On first use, use the term: UFA (Unsuitable For Analysis). Specify cause for UFA result in final report, but not on the EHLB reporting sheet.

Examples: Sample XXOOO Tube Front: MITC 2.085 µg/mL ± 0.052 µg/mL.
Sample XXOOO Tube Rear: ND (Not Detected). LOD (Limit of Detection) 0.030 µg/mL.
Sample XXOOO: MITC 6.255 µg/Sample. ± 0.156 µg/Sample

Sample XXX00: MITC < LOQ (Limit of Quantitation), LOQ 0.025 µg/mL
Sample OOXXX: UFA (Unsuitable For Analysis)

11.5.5 Desorption Efficiency Correction. Report results uncorrected for Desorption Efficiency. Supply D.E. data to contracting agency.

12. Data Assessment and Acceptance Criteria

Meet with Quality Control staff, and examine all results, including acceptability of MLOD, TSD bead performance (operating current(s) and initial optimization data, acceptability of Q.C. and check standard injections, linearity of daily calibration curves, and quantitations of samples to fall within calibrated range. Once review and approved, release data to supervisor. Prepare copies of all related reports, originals to file, copies to supervisor.

13. Corrective Actions

Follow the protocol as described in Corrective and Preventative Action Report SOP (CPA/R0).

14. Method Performance

Describe and document the basis for interlaboratory or EHLB generated method performance data with regard to:

14.1 Accuracy and precision

14.2 Accuracy and precision control limits

14.3 Method Detection Limit
0.0014 µg/mL ± 0.0004 µg/mL, 22 Oct. 1999.

Reporting Limit
5.0 µg/mL – 0.025 µg/mL

14.4 Desorption Efficiencies

Performed 26 Oct. 1999

67.1 % ; 5.0 µg/mL – 0.025 µg/mL (includes blank)
63.7% : 1.0 µg/mL – 0.025 µg/mL (includes blank)

15. Waste Management

At the performance limits, µg/mL, MITC is considered sufficiently diluted to make the solvent Carbon Disulfide the greater hazard. Dispose of all MITC related materials, including samples, standards and quality controls prepared in CS_2, by discarding into a "Carbon Disulfide Waste Only" labelled glass bottle (for example, an emptied CS_2 solvent bottle). Filled bottles are sent to facility storage following the Health and Safety facility protocols specified by the DHS Toxicologist, Deputy State Fire Marshall, and EHLB Health & Safety Committee.

16. References

Document applicable EHLB procedures and other reference sources.

17. Approvals

Document the preparer, reviewer, and management approval of the standard operating procedure with each individual's signature and date.

4. Approvals

Prepared by: _____ Date:

Reviewed by: _____ Date:

Approved by: _____ Date:

Additional comments:

1) Significant Figure determination, including standardization of rounding rules needs to be addressed.

2) Unit standardization rules (for both in-house good communication, and for reporting results on forms for clients) need to be addressed. Compliance to NIST Special Publ. 811, pgs. v-vi (attached), is recommended.

P.L. 26 Feb 99

Table 1a. MITC Trapping Efficiency Study Performed
by the Department of Health Services Laboratory
at a flow rate of 2 L/min for 16 hours - November 1999

		Results		
Sample I.D.	Spike Level (ug)	Front (ug)	Back (ug)	Recovery (%)
fortified	300	81.5	<LOQ[e]	27
fortified	300	93.0	<LOQ	31
fortified	3000	784.2	805.1	53
fortified	3000	796.1	829.2	54
trip spike	300	227.0	ND	76
trip spike	3000	2230.0	ND	74
trip blank		ND	ND	
trip blank		ND	ND	
trip blank		ND	ND	

Table 1b. MITC Trapping Efficiency Study Performed
by the Department of Health Services Laboratory
at 1 and 2 L/min flows for 16 hours - December 1999

			Results		
Flow Rate (L/min.)	Sample I.D.	Spike Level (ug)	Front (ug)	Back (ug)	Recovery (%)
2	fortified	1000	710.6	112.3	82
2	fortified	1000	644.0	ND	64
2	fortified	3000	1931.6	525.1	82
2	fortified	3000	2213.7	110.1	77
1	fortified	1000	851.9	ND	85
1	fortified	1000	710.6	112.3	82
1	fortified	3000	2138.4	ND	71
1	fortified	3000	2204.8	90.6	77
	trip spike	1000	739.0	ND	74
	trip spike	1000	655.8	ND	66
	trip spike	3000	1955.3	ND	65
	trip spike	3000	2217.5	ND	74

a. Fortified sample run on an air sampler in the field.
b. Limit of Quantitation = 0.100 ug
c. None detected = less than 0.030 ug
d. Trip spikes accompany field samples but are not run on air samplers.
e. Laboratory spikes are prepared in the lab when trip and fortified spikes are prepared, but stored in the lab. These are extracted and analyzed with the field samples when they return to the lab.

Table 2a. MITC Desorption Efficiency Data from the Department of Health Services Laboratory. Data generated November - December, 1999.

Spike Level (ug)	Results Front (ug)	Back (ug)	Recovery (%)
150	94.4	ND	63
150	114.2	ND	76
3000	2240	ND	75
3000	2235	ND	75
300	217.6	ND	73
300	228.1	ND	76
3000	2400	ND	80
3000	2540	ND	85
1000	636.3	ND	64
1000	690.1	ND	69
3000	2186.9	ND	73
3000	2203.8	ND	73
		Average	73
		Std Dev.	6

Table 2b. MITC Desorption Efficiency Data from the Department of Health Services Laboratory. Data generated January - February, 2000

Spike (ng)	Result (ng)	Recovery (%)
1000	734.0	73.4
1000	730.1	73.0
500	351.5	70.3
500	350.0	70.0
100	66.4	66.4
100	66.5	66.5
50	31.2	62.4
50	30.8	61.6
25	17.8	71.2
25	17.7	70.8
0	0	
0	0	
	Average	68.6
	Std. Dev.	4.2

Department of Health Services Laboratory
Summary: MITC MDL by GC-NPD

n	Peak Candidate	Conc ng/mL	Conc ng/smpl	**Mean Conc ng/smpl**	Rel Std Dev (%)
1	100 ng/sample #3	22.24	66.73	67.00	0.55
	100 ng/sample #3	22.42	67.26		
2	100 ng/sample #7	25.30	75.91	76.18	0.51
	100 ng/sample #7	25.49	76.46		
3	100 ng/sample #8	23.97	71.91	71.64	0.53
	100 ng/sample #8	23.79	71.37		
4	100 ng/sample #6	22.48	67.43	67.52	0.18
	100 ng/sample #6	22.54	67.61		
5	100 ng/sample #4	22.38	67.13	67.06	0.16
	100 ng/sample #4	22.33	66.98		
6	100 ng/sample #9	22.27	66.81	67.17	0.74
	100 ng/sample #9	22.51	67.52		
7	100 ng/sample #1	24.29	72.86	73.05	0.37
	100 ng/sample #1	24.41	73.24		
8	100 ng/sample #2	24.25	72.76	72.97	0.40
	100 ng/sample #2	24.39	73.18		
9	100 ng/sample #5	22.30	66.90	66.76	0.30
	100 ng/sample #5	22.21	66.62		
10	100 ng/sample #10	21.30	63.90	64.27	0.81
	100 ng/sample #10	21.55	64.64		
	Averages	23.12	69.36	69.36	
	%RSD	5.35	5.35	5.48	
	SD		3.71	3.80	
	DOF			9	
	MDL (ng/sample)			**12.36**	
	MQL (ng/sample)			**37.08**	